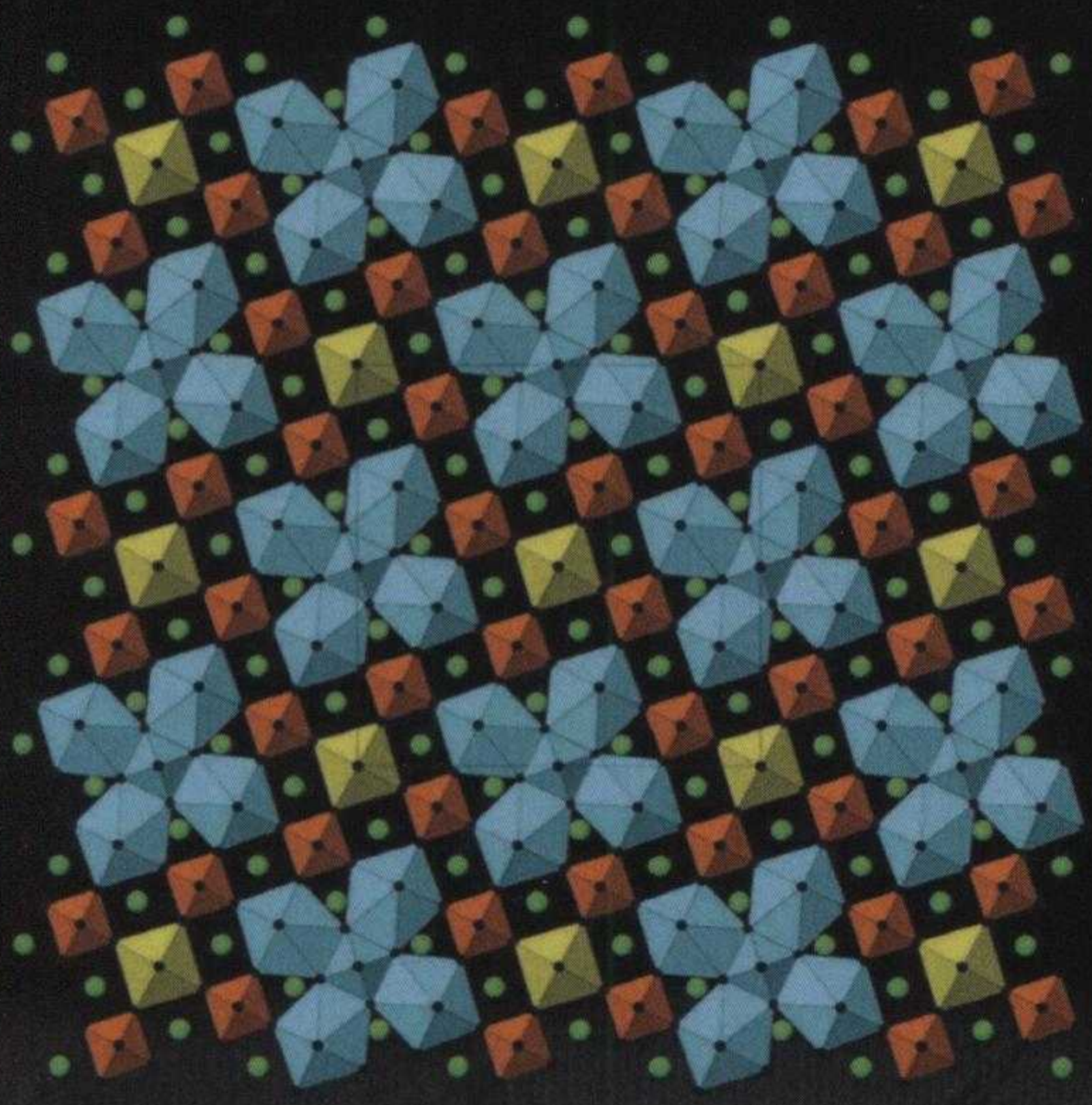
ELSEVIER

# Fluorine
## A Paradoxical Element



Alain Tressaud

Progress in Fluorine Science Series

Series Editor Alain Tressaud

## Progress in Fluorine Science Series

Volume 1 – *Photonic and Electronic Properties of Fluoride Materials*
A. Tressaud, K. Poeppelmeir, Eds.

Volume 2 – *New Fluorinated Carbons: Fundamentals and Applications*
O. Boltalina, T. Nakajima, Eds.

Volume 3 – *Modern Synthesis Processes and Reactivity of Fluorinated Compounds*
H. Groult, F. Leroux, A. Tressaud, Eds.

Volume 4 – *Fluorine in Life Sciences: Pharmaceuticals, Medicinal Diagnostics, and Agrochemicals*
G. Haufe, F. Leroux, Eds., ISBN: 9780128127339.

Progress in Fluorine Science Series - Volume 5

# Fluorine

## A Paradoxical Element

*Alain Tressaud*
**ICMCB-CNRS, University Bordeaux,**
**Pessac, France**

ELSEVIER

Elsevier
Radarweg 29, PO Box 211, 1000 AE Amsterdam, Netherlands
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, United Kingdom
50 Hampshire Street, 5th Floor, Cambridge, MA 02139, United States

© 2019 Elsevier Inc. All rights reserved.

Cover image credit: From F. J. Zúñiga, A. Tressaud, J. Darriet, The low-temperature form of $Rb_2KCrF_6$ and $Rb_2KGaF_6$: the first example of an elpasolite-type structure with pentagonal bipyramid in the B-sublattice, 176, 3607–3614, Journal of Solid State Chemistry, Copyright Elsevier (2006).

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Details on how to seek permission, further information about the Publisher's permissions policies and our arrangements with organizations such as the Copyright Clearance Center and the Copyright Licensing Agency, can be found at our website: www.elsevier.com/permissions.

This book and the individual contributions contained in it are protected under copyright by the Publisher (other than as may be noted herein).

## Notices

Knowledge and best practice in this field are constantly changing. As new research and experience broaden our understanding, changes in research methods, professional practices, or medical treatment may become necessary.

Practitioners and researchers must always rely on their own experience and knowledge in evaluating and using any information, methods, compounds, or experiments described herein. In using such information or methods they should be mindful of their own safety and the safety of others, including parties for whom they have a professional responsibility.

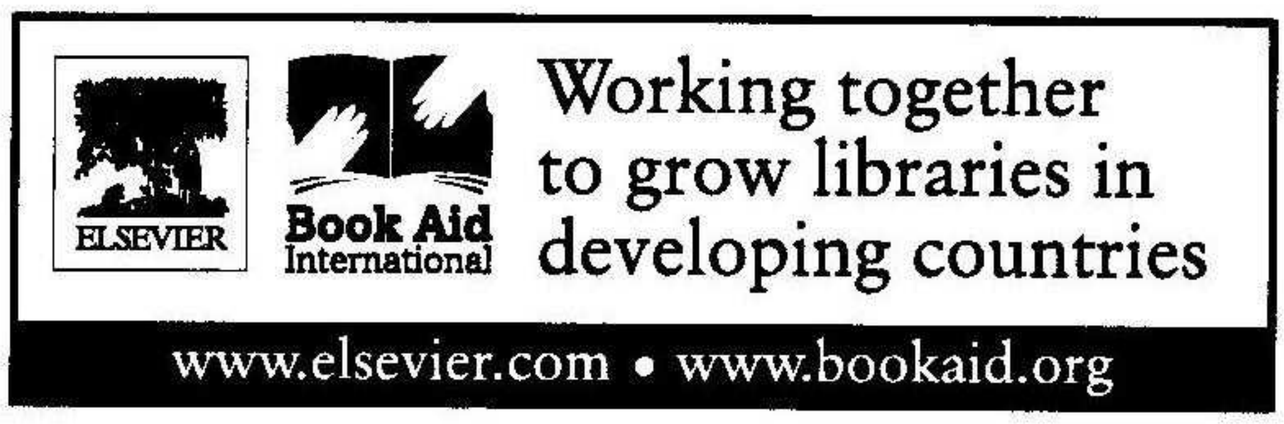
To the fullest extent of the law, neither the Publisher nor the authors, contributors, or editors, assume any liability for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions, or ideas contained in the material herein.

**Library of Congress Cataloging-in-Publication Data**
A catalog record for this book is available from the Library of Congress

**British Library Cataloguing-in-Publication Data**
A catalogue record for this book is available from the British Library

ISBN: 978-0-12-812990-6

For information on all Elsevier publications visit
our website at https:/www.elsevier.com/books-and-journals




*Publisher:* Candice Janco
*Acquisition Editor:* Emily McCloskey
*Editorial Project Manager:* Katerina Zaliva
*Production Project Manager:* Omer Mukthar
*Cover Designer:* Katerina Zaliva

Typeset by SPi Global, India

# Contents


**Foreword** ix
**Introduction** xi

**1 History and milestones of fluorine and fluorinated products through the centuries** 1

1 History and uses of fluorinated minerals 2
2 Fluorine dating in archeology 14
3 The true nature of the Roman murrhine through a critical lecture of Pliny the Elder's "Naturalis Historia" 31
4 Georgius Agricola, the father of mineralogy and creator of the word "fluoride" 36
5 In search of the missing halogen, from the Renaissance to 1886 41
6 The isolation of fluorine on June 1886 by a pharmacist and chemist: Henri Moissan 45
7 Physical chemical characteristics of fluorine 49
8 Some breakthroughs in the development of fluorine and fluorinated products throughout the 20th century 52

**2 Fluorine, a key element for the 21st century** 77

1 Advances in organic fluorine chemistry 78
2 Advances in new fluorination routes, surface functionalization, and nanosized fluorocompounds 84
3 Industrial applications of fluoride minerals, gases, and inorganic fluorinated products 99
4 Uses of fluorides in photonics 107
5 Uses of fluorides in electronics and other modern technologies 119
6 Contributions of fluorinated products in medicine, pharmacy, and biotechnologies 132
7 Plant protection products and insecticides 149

**3 Fluorinated compounds in our environment: Fluorine, friend or foe for humanity?** 151

1 Genesis and cosmo-chemistry of fluorine 152
2 Fluorine and our atmosphere 164
3 Fluorine and the lithosphere 192

4 Fluorine, friend or foe for human health? **220**
5 Contamination and physiological effects of fluoride on living organisms **227**
6 Improving the quality of drinking water by defluoridation **235**

**Conclusion** **241**
**Appendix** **245**
**Index** **247**
**Acronyms** **255**
**Acknowledgments** **259**

# Foreword

The history of fluorine becomes lively when Alain Tressaud reports on the Section 1 of the book with the title, "Fluorine: A Paradoxical Element." Indeed fluorine has a Janus head with two faces, and the author elegantly shows its pros and cons. This is a real masterpiece of a book. Sections 2 and 3 are entitled, "Fluorine: A Key Element of the 21st Century," and "Fluorinated Compounds in Our Environment." On the one hand, both chapters demonstrate how important fluorine compounds contribute to the technical development of our daily life. On the other hand, we face the problem of contamination from fluorine-containing compounds. In principle, this has already been known since the Swiss medical doctor Paracelsus (1493–1541) wrote, "All things are poison and nothing exists without poison, alone the amount is responsible for being a poison." Presently, everyone faces daily contamination of the air with increasing amounts of exhaust gases from burning coal and gasoline, or learns from the newspaper about the contamination of water with nitrates and large amounts of plastic in the oceans. Huge consumer demand for products creates an enormous problem today and for the future. Alain Tressaud shows this convincingly in his discussion of the development of fluorine-containing products. Therefore, this book is a very valuable and key contribution and an eye-opener for the researcher, producer, and consumer interested in sustainable development. I hope that this book will not only be read by fluorine experts but also distributed to others who are involved in research and environmental issues.

**Herbert W. Roesky**
**Göttingen, Germany**

# History and milestones of fluorine and fluorinated products through the centuries

1

## Chapter Outline


**1 History and uses of fluorinated minerals 2**
- 1.1 Fluoride crystals as gemstones substitutes 4
- 1.2 Fluorinated powders as "therapeutics" 6
- 1.3 Uses of fluorspar minerals as pigments 6
- 1.4 Uses of fluorspar as ornaments and in decoration items 6
- 1.5 Middle ages forgeries: fossilized mastodon tusks sold as synthetic "turquoise" 7

**2 Fluorine dating in archeology 14**
- 2.1 Relative dating of bones and skeletal remains 16
- 2.2 Dating archeological lithic artifacts by fluorine diffusion 24

**3 The true nature of the Roman murrhine through a critical lecture of Pliny the Elder's "Naturalis Historia" 31**

**4 Georgius Agricola, the father of mineralogy and creator of the word "fluoride" 36**

**5 In search of the missing halogen, from the Renaissance to 1886 41**

**6 The isolation of fluorine on June 1886 by a pharmacist and chemist: Henri Moissan 45**

**7 Physical chemical characteristics of fluorine 49**

**8 Some breakthroughs in the development of fluorine and fluorinated products throughout the 20th century 52**
- 8.1 The rapid growth of the aluminum industry 53
- 8.2 The rise and fall of CFC 58
- 8.3 The story of Teflon and fluoropolymers 68
- 8.4 Fluorine, a decisive element in the nuclear cycle 72


Until the dawn of technological (al)chemistry, the value of many minerals was widely recognized and exploited without suspecting the nature of the element at the origin of these properties, for example, aluminum in alum and fluorine in fluorite (fluorspar or flußspat). It can be noted that the name of these two elements finally resulted from the properties of these minerals: i.e. the element that flows for F and the metal from clay for Al. The word fluorine (*fluores* in Latin) appeared for the first time in 1530 in a book written by G. Agricola, but long before that, the melting properties (or "flux") of the fluorinated minerals had been identified, and the beauty and reputed magical properties of these crystals had fascinated many ancient civilizations. Some examples will help us to follow the history of fluorine and fluorinated minerals throughout the centuries: fluoride crystals as gemstones, the real history of the murrhine vases of

**Fluorine. https://doi.org/10.1016/B978-0-12-812990-6.00001-5**
© 2019 Elsevier Inc. All rights reserved.

Imperial Rome, fossil fluorapatites used as synthetic turquoises by the monks of the Middle Ages, description of the use of cryolite in smelting by G. Agricola during the Renaissance period. An important place will be devoted to the fierce competition between the greatest scientists of the 18th and 19th centuries to characterize fluorocompounds and isolate the $F_2$ element, a competition that allowed exceptional discoveries, culminating in the isolation of fluorine by Henri Moissan in 1886.

## 1 History and uses of fluorinated minerals

In very ancient times, beautiful Egyptian ladies were using fluoride crystals as ornaments, especially fluorite. Carved figurines and beetles have been found during archeological excavations, hundreds of fluorite seals have been found in Aegean sites of the Late Bronze Age,[1] and a multitude of various objects were made over many centuries in ancient China. At Moncy-St-Pierre (France), necklaces with fluorite beads accompanied wealthy Merovingians in their last resting places (6th–7th centuries). In Amerindian civilizations, fluorite crystals were likely cut for religious reasons, as evidenced by the figurine of a sitting man discovered in the Angel pit site in Indiana (United States), which could have been an idol for the main temple.[2] The importance of murrhine vases in Imperial Rome will be later mentioned. As such, it is said that Hadrian would have launched the conquest of northern England mostly to appropriate deposits of "Blue John" fluorspar (Fig. 1), a banded mineral with

**Fig. 1** Banded fluorite crystal from Castleton, United Kingdom.
Photo Michael Vickers, Used with permission from Michael Vickers.

[1] A. Dickers, Die spätmykenischen Siegel aus weichem Stein. VLM Verlag Marie Leidoerf GmbH, Rahden, Germany (2001).

[2] C. R. Stafford, Prehistoric People of Indiana, INARNG Integrated Cultural Resources Management Plan A187, Indiana State University (2001).

extremely bright colors that was—and still is—extracted in Cumbria[3] (see – "Etymology: the 'fluid' rather than 'destructive' ").

## Etymology—The "fluid" rather than "destructive"

Many minerals have been recognized and used for centuries without suspecting what element was at the origin of their properties. However, the names attributed to these products corresponded most times to the real nature of the element. This is the case for fluorine in fluorspar ores (fluorite, $CaF_2$), as for aluminum in alum. Thus, the origin of the word "fluorine" comes from the Greek root "fluo-" (φλυω: "sink") and the Latin "fluorine" ("fluere," or "flow"). Saxon miners named fluorite ores "fluβspat" (also "flosse," "flüsse," "fluss-spaht," "spatum vitreum," or "calx fluorata") due to the properties of these crystals (from "fluss," or "flow," and "spat," or "spar," that derived from the Old German "spalten," meaning "crack," or "cleave"). They also gave more colorful names like berg-bluhme or metall-bluhme ("bluhmen," or "flower" in Old German), because of the beauty of their blooms. When Agricola translated in Latin these German names for *De Natura Fossilium* and *Bermannus, re metallica of dialogus sive*, he chose "fluores" probably because of the melting properties of these crystals, but one can imagine that he might have also been influenced by the proximity of the Latin words "fluores" and "flores" ("flowers").

The symbol "F" for fluorine appeared in an article in 1814, but until the second half of the 19th century, it was the symbol "Fl" which was most commonly used. It may be noted that in some Anglo-Saxon texts, the misspellings "flourine" or "flourspar" are still used. In his letter to Davy, dated August 26, 1812, Ampere, having realized that hydrofluoric acid contained no oxygen, replaced the word "oxy-fluorique" with a new proposal, the French word, "fluorine." It's Davy who released this name in the United Kingdom the following year by using exactly the word proposed by Ampere. But on a second occasion, Ampere (to account for the aggressive nature of hydrofluoric acid) proposed replacing the word fluorine with "phtore" or "phthore." This term (coming from the Greek *Φθόριος* and meaning "destructive") seemed more appropriate to account for the properties of its derivatives: "I chose the name phtore, which takes, in both noun and adjective form, the meaning 'deleterious,' which has the power to destroy, corrupt."[4]

Although this name was in good agreement with the nomenclature of the other halogens, it was not accepted by the scientific community at the time, partly because of the influence of the journal "Annals of Philosophy," which favored the word fluorine. Today, this term is still mostly used, including, for example, in Japan where フッ素 ("fusso") is associated with the flow concept. However, in a book published in Russia around the same period, *Osnovaniya Obshchei Khimii*, the author, G.H. Hess, proposed the name "ftor," and since that time Russian chemists call the element *Фтор* which is also the case in the Greek-speaking community: *Φθόριον*. Now, all names used worldwide when speaking of this element (i.e., hydrofluoric, fluorine, or phtor) were initially proposed by Ampere. Note that the word "fluorescence" is also derived from the same root.[5]

[3] "Blue John" fluorspar crystals (name derived from the French word "bleu-jaune"), with beautifully colored strips, are extracted since centuries in the Hope Valley, near Castelton, Derbyshire, in the Northern part of England.

[4] A. M. Ampere, "D'une classification naturelle pour les corps simples," Ann. Chim. Phys. 2 (1816) 5–32.

[5] The fact that some fluorite crystals ($CaF_2$) became luminescent after being heated had already been noticed by J.L. Elsholtz in Vienna in 1676, and this characteristic was studied in 1824 by the German mineralogist F. Mohs (1773–1839). It was in 1852 that the Irish scientist G.G. Stokes (1819–1904) named this property fluorescence: "I am also inclined to coin a word, and call the appearance fluorescence, from fluorspar, as the analogous term opalescence is derived from the name of a mineral."

## 1.1 Fluoride crystals as gemstones substitutes

Due to their richness and shimmering colors, crystals of fluorite (fluorspar) and apatite, the most well-known of the fluorinated gemstones, were often confused—accidentally or intentionally—with more valuable precious stones. Because the purple, green, or blue varieties of fluorites ("fluorinated violaceo color") can be confused with amethyst, emerald, or sapphire, their names were often given as "false amethyst," "false emerald," or "false sapphire" (in Latin: *pseudo-amethystus, pseudo-smaragdus, pseudo-hiacynthus*)[6] (Fig. 2A). Dark purple fluorspar, called "bull beef" by workmen, may be changed, by heat, to a rich amethyst tint. Nevertheless, their use in jewelry is quite limited, because these stones can be easily scratched, which is not the case with another fluorinated crystal, topaz. In addition, because of their fragility, fluorite crystals are very difficult to process and may require the use of resins during cutting operations (see later).

In addition to fluorites and apatites, some other fluorinated minerals have been used as semi-precious stones (Fig. 2B), such as:

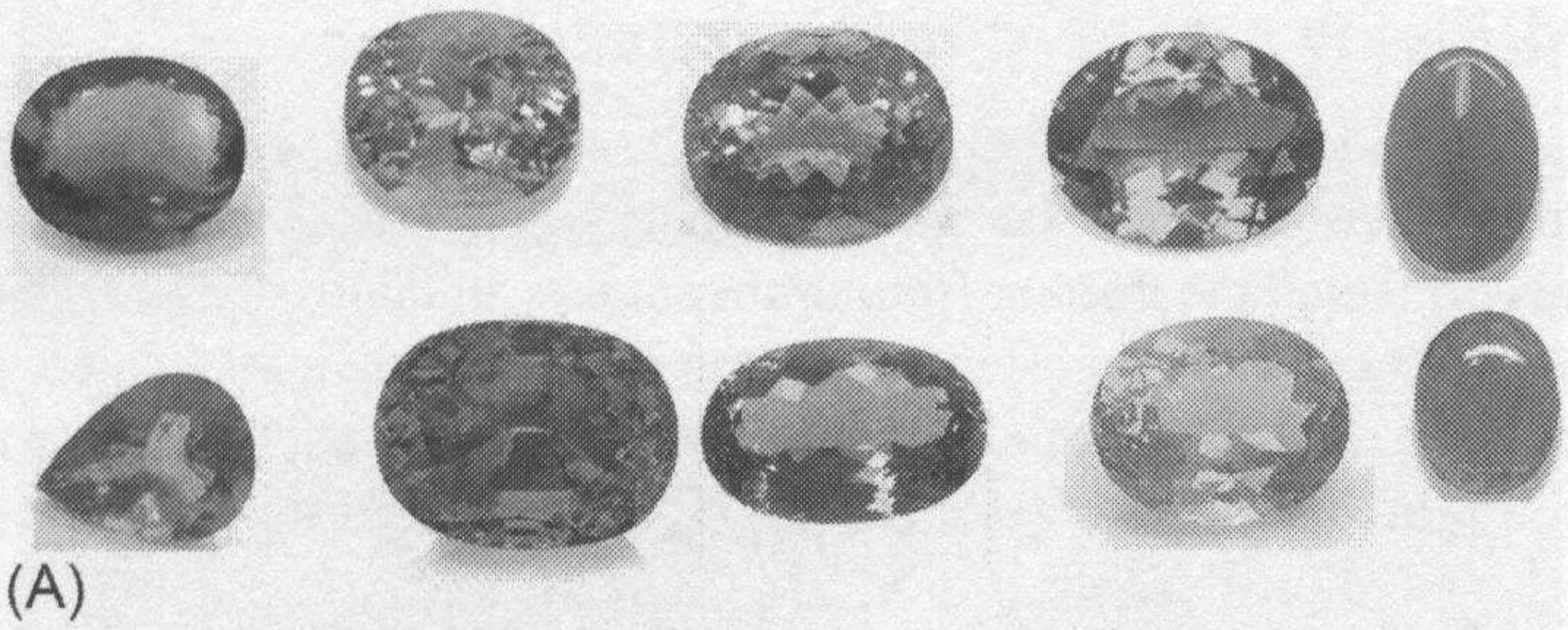
- *Tourmaline*: $NaX_3Al_6(BO_3)_3(Si_6O_{18})(OH, F)_4$ compounds belong to the group of cyclosilicate minerals[7] (Dana class 61.3.1; Dana 1997),[8] in which tetrahedra form $(Si_6O_{18})^{-12}$ rings. These crystals usually exhibit pyroelectric properties. The fluorine content depends on the nature of the cations present in the X site, and also on the Fe/Fe+Mg) ratio. The color of these crystals is strongly influenced by the nature of the X cation: green or transparent for X=Li or Al (indicolite or liddicoatite), brown to transparent for X=Mg (Dravite),[9] or even black for X=Fe or Mn in shorlites. In buergerite, the OH groups are replaced by three O and one F. This leaves a space open for one more positive charge, which is compensated for by 3 $Fe^{3+}$ ions, which leads to the formula, $NaFe^{3+}{}_3Al_6(BO_3)_3Si_6O_{21}F$. This mineral has a color that is bronze to brown and black, with a hardness of 7 Mohs. The best tourmaline gems come from granitic pegmatites (Brazil, Madagascar, Mozambique).
- *Topaz*: $Al_2SiO_4$ $(F, OH)_2$ which belongs to the nesosilicates group (Dana 52.3.1.1 class) in which $SiO_4$ tetrahedra are independent and contain some O not bound to Si. The crystals may be transparent or blue, green, yellow, or orange. They are found in eruptive acidic deposits, and their size can reach several tens of kg (Brazil, Russia) (Fig. 2C).
- *Jadeite-nephritis*: $Ca_2(Mg,Fe)_5Si_8O_{22}(F,OH)_2$ which are tremolite varieties (Dana 65.1.3c.1 class). The color of these minerals varies from yellow to green and very dark green. In many civilizations, sculptures were carved in these minerals, such as this Olmec mask (Mexico, 1250–900 BC) (Fig. 2D).

[6] "The 'fluatée' lime (i.e., fluorite crystals) is, among all the stony substances, the one that most lent to the effects of the coloring actions of metal oxides. Also, the illusion that tends to produce the resemblance between the hues that adorn these crystals with those of stones called gems, suggested their names as false ruby, false sapphire, false emerald etc., that the ancient mineralogists had given, according to the diversity of its colors," V. Haüy, Traité de Minéralogie (1822).

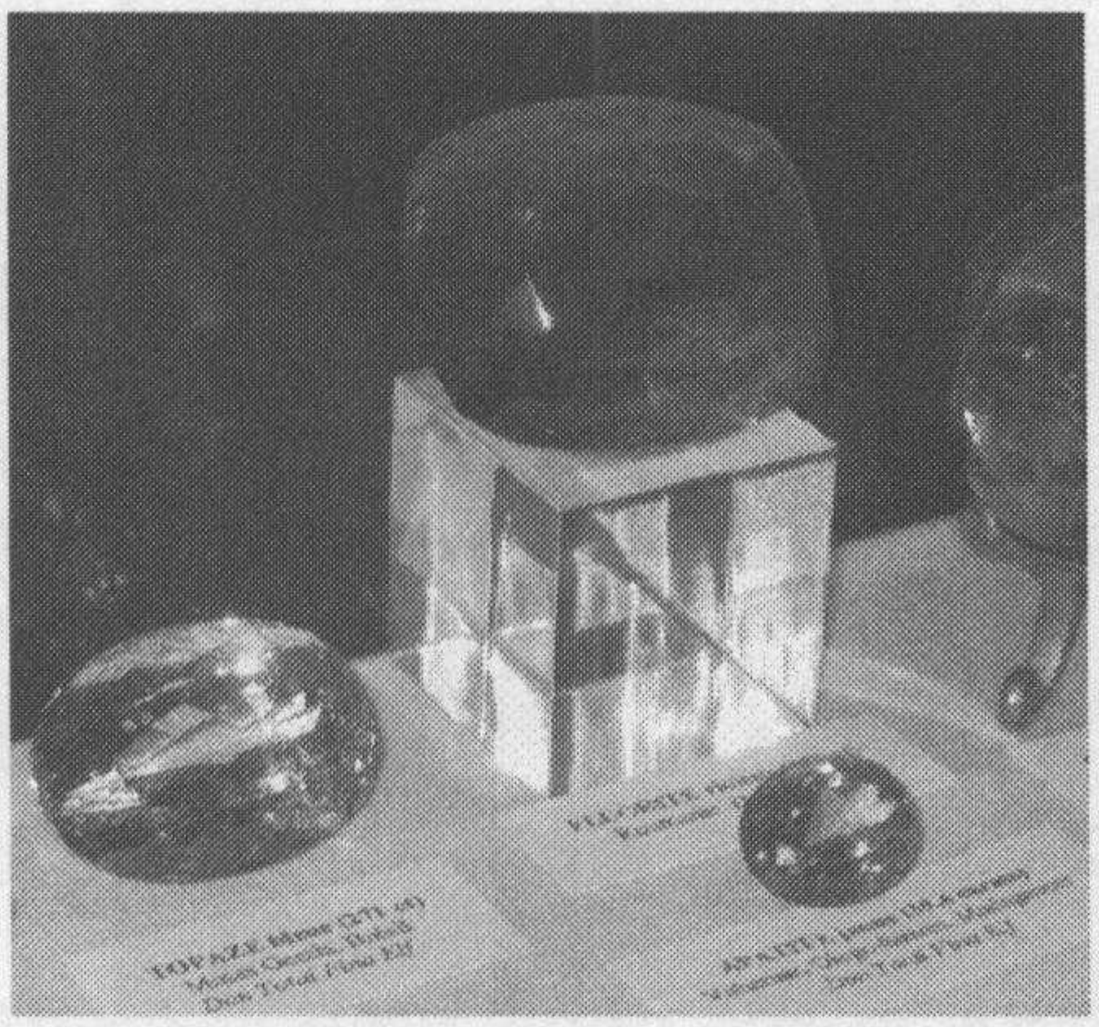
[7] F.C. Hawthorne, D.J. Henry, Classification of the minerals of the tourmaline group, *Europ. J. Mineral.*, **11** (1999) pp. 201–215.

[8] R. V. Gaines et al., Dana's New Mineralogy, 8th Edition, John Wiley & Sons, New York (1997).

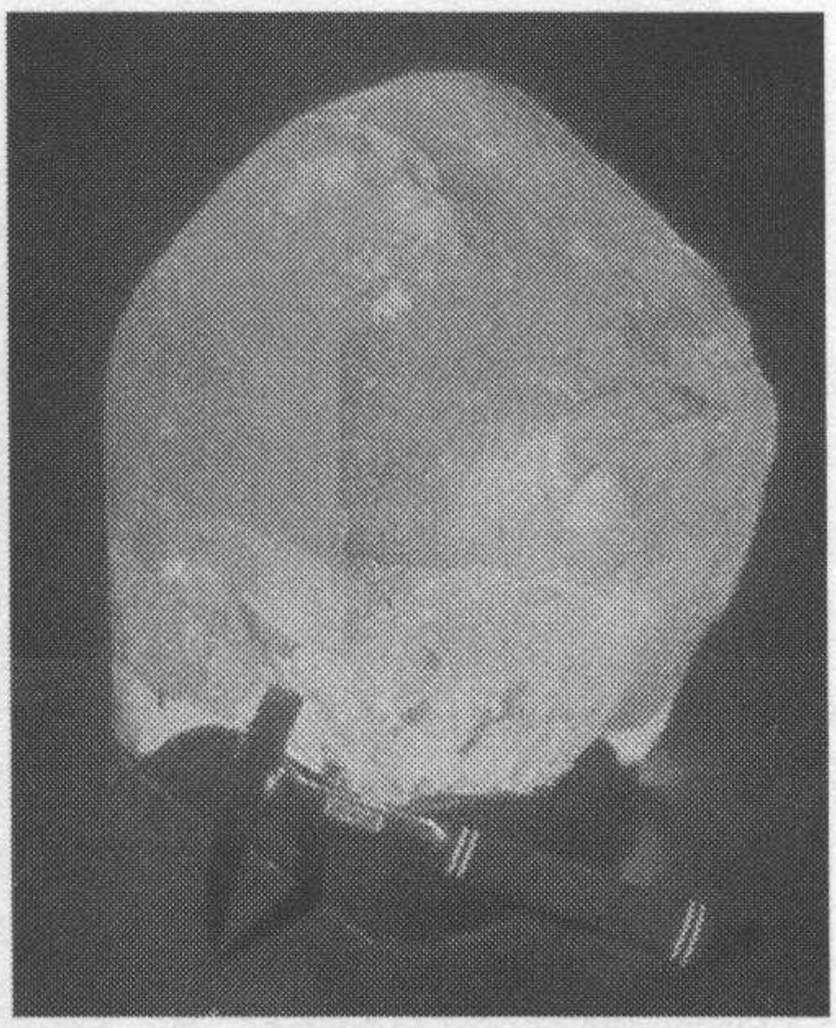
[9] I. Baksheev, O. Kudryavtseva, Compositions of hydrothermal dravitic tourmalines from Ural, *Geophys. Res. Abst.* **5** (2003) p. 262.



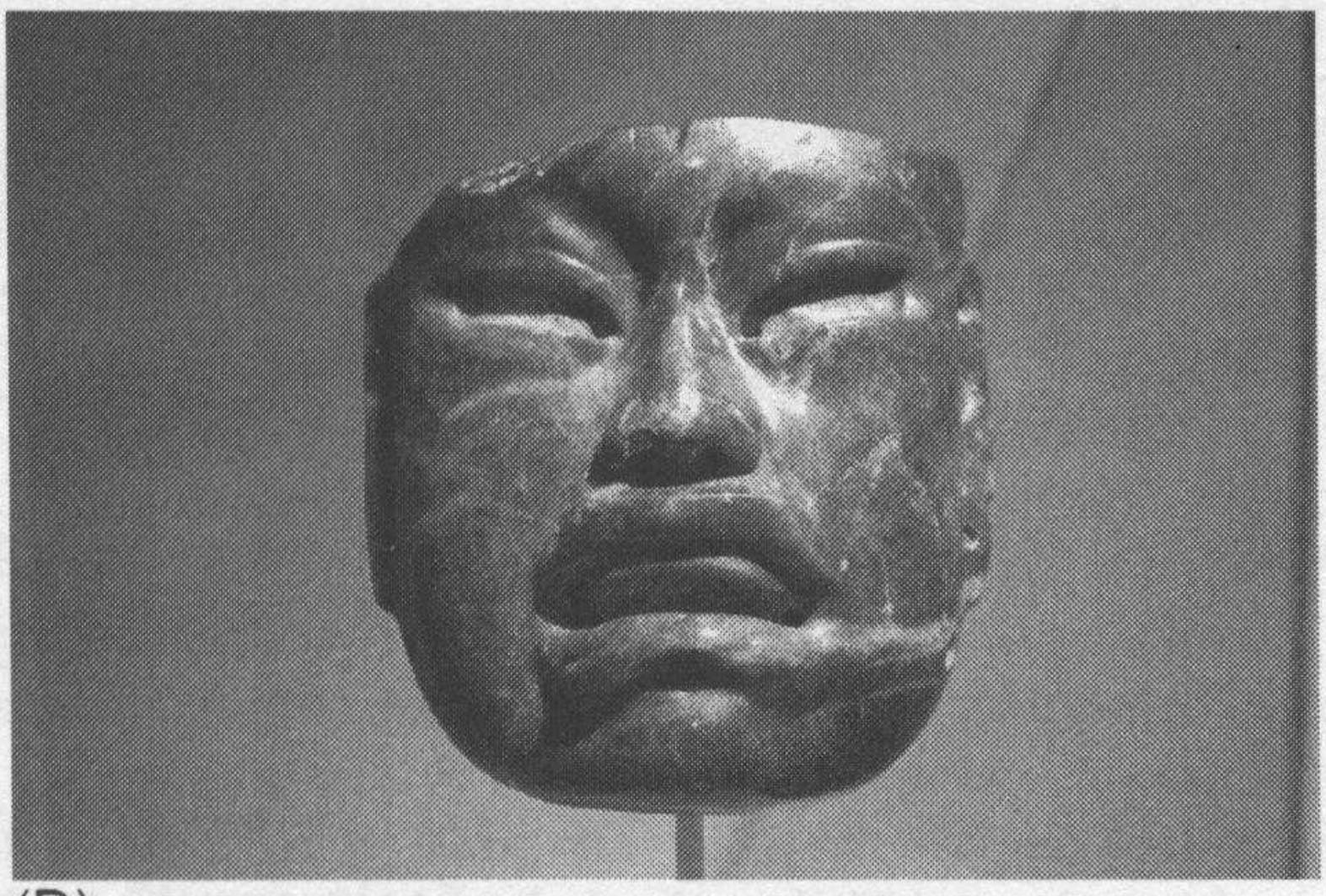
(A)



(B)



(C)



(D)

**Fig. 2** Fluoride gemstones: (A) fluorite, tourmaline, topaz, apatite, jadeite; (B) topaz, fluorite, apatite from MNHN, Paris; (C) 150 kg topaz, Museum Univ., Florence; (D) Jadeite Olmec mask.

## 1.2 Fluorinated powders as "therapeutics"

It was long assumed that fluorite crystals possessed healing, even magical, powers. The ancient Romans believed that drinking alcoholic beverages in containers cut from such crystals protected the drinker from drunkenness, and until the 18th century, powdered fluorite crystals were ingested in water to reduce the pain associated with kidney stones. In ancient times, it was thought that fluorspar had a marked ability to relax the muscles, could produce a sour taste though simply held in the hand, and sometimes induced a somnambulistic state.[10]

## 1.3 Uses of fluorspar minerals as pigments

Purple fluorite powder was used in northern Europe as a pigment on polychromic wooden sculptures at the end of the Gothic and early Renaissance periods. Given the places where those pigments were found (Saxony, Tyrol, Switzerland and Silesia), the spectrum of their colors was very wide, including violet and darker colors of fluorspar minerals from Wölsendorf mines. Because of the weak hue of these powders, they were used to reinforce the color effect.[11] Similarly, $CaF_2$ could be detected by SEM and EPMA in Chinese cloisonné enamels from the 16th and 17th centuries.[12]

## 1.4 Uses of fluorspar as ornaments and in decoration items

Around Castleton, in the rolling landscape of Derbyshire Peak District in northern England, a unique type of fluorite ore, the "Blue John," has been found for a couple thousand years by miners looking for lead veins. As written by T. Thomson (1773–1852), "The mineral called flourspar, and in this country frequently distinguished by the name of Derbyshire spar, is so common in lead mines, and is so beautiful in consequence of its transparency, its fine colours, and the large size of its cubic crystals, that it must have early attracted the attention of mankind. There can be little doubt that it is mentioned both by Theophrastus and Plinius under the name of false-emerald." This unique type of fluorite is formed of alternating strips of violet, yellow, or gray (see Fig. 1). Today, the mine of Treak Cliff Cavern still produces 500 kg of Blue John fluorite per year. There are up to 14 different types of banded fluorites, and because of their exceptional beauty, they have been used as decoration since the 18th century. Among these, we can cite chimneys by the great architect R. Adam (1728–92), Boulton's work of ormolu, and Vallance's obelisks and vases. Such fluorite objects can also be found in Windsor Castle, the White House, or the Vatican.[13] Note that some

[10] A. R. Bliss, The ancient medicinal uses of gems and precious stones, J. Amer. Pharmac. Assoc. Vol. XXV, (1936) pp. 544–545.

[11] Richter M., Hahn O. Fuchs R., Purple fluorite: a little known artists' pigment and its use in Late Gothic and Early Renaissance painting in northern Europe, Studies in Conservation, **46** (2001) pp. 1–13.

[12] Henderson J., Tregear M., Wood N., The technology of sixteenth- and seventeenth-century Chinese cloisonne enamels, *Archaeometry*, **31** (1989) 133–146.

[13] Ford T. D., Proc. Yorksh. Geol. Soc. **30** (1955) pp. 35–60.

**Fig. 3** Fluorite balusters from Voltennes (Burgundy, France) at Opera Garnier, Paris (SAGA, Société amicales des géologues Amateurs, France, https://www.saga-geol.asso.fr/).

balusters of the Opera Garnier in Paris are made from blocks of fluorite coming from the mine in Voltenne (Saône et Loire)[14] (Fig. 3).

## 1.5 Middle ages forgeries: Fossilized mastodon tusks sold as synthetic "turquoise"

During the Middle Ages, a material of a beautiful turquoise-blue color was commonly used by the monks of Cistercian monasteries in France to decorate religious objects such as cross reliquaries. For example, in the collections of the National Museum of the Middle Ages of Paris, such stones are embedded in the reliquary of the True Cross made in Limoges in the 12th century (Fig. 4). Since the 19th century, it was recognized

[14] Joseph D. Etude géologique et minéralogique des gisements de fluorine de Voltenne et de Maine, 3rd cycle Thesis, Orléans, France (1974).

**Fig. 20** The "Crawford" cup, Imperial Roman fluorite/murrhina cup (GR 1971.4-19.1). Reproduced with the British Museum permission, London. ©The Trustees of the British Museum.

Natural History. Note that another translucent fluorspar cup is also present in the Ashmolean Museum in Oxford.[67]

Figurines and various objects have continued to be carved in fluorite crystals over the centuries, as evidenced by this pair of urns from the late eighteenth century (Fig. 21). Note that during investigations that led Henri Moissan to isolate fluorine, the scientist might have used an electrolysis cell cut from a large block of fluorite crystal (fluorspar) (Fig. 22). The interest of such a material is that it does not react with fluorine and fluorinated gases. However, it is not proven that Moissan actually used this type of cell, for airtight reasons.

## 4 Georgius Agricola, the father of mineralogy and creator of the word "fluoride"

The attractive properties of fluorspar ores ($CaF_2$) as fluxes in metallurgy had begun to be recognized from the Middle Ages. These additives were called "Flußspat" by German miners. It is said that that this use was mentioned for the first time by Basilius Valentinus in the late 15th century.[68] But it was G. Agricola who brilliantly described the importance of these fluorinated ores. Georg Bauer was born in Saxony in 1494. His study of the humanities led him to various European universities, first in Leipzig, then in Bologna and Padua. During this period, he Latinized his name to Georgius Agricola. In a Europe that began to be shaken by the ideas of the Reformation, his wisdom and openness allowed him to approach the great minds of his time, especially D. Erasmus. Very influenced by the ideas of his mentor, Agricola remained loyal to the Catholic Church, but in a spirit of openness and tolerance. From 1526, Agricola

[67] M. Vickers, Hamilton, geology, stone vases and taste, J. Hist. Collect. **9** (1997) 263–274.

[68] Gmelins Handbuch der anorganischen Chemie, 8. Auflage, System-Nr. 5, "Fluor," Verlag Chemie, Leipzig/Berlin 1926, p. 1.

**Fig. 21** A pair of fluorite urns (XVIIIth century).
Reproduced with permission of Galerie du Rhône, Sion, Switzerland.

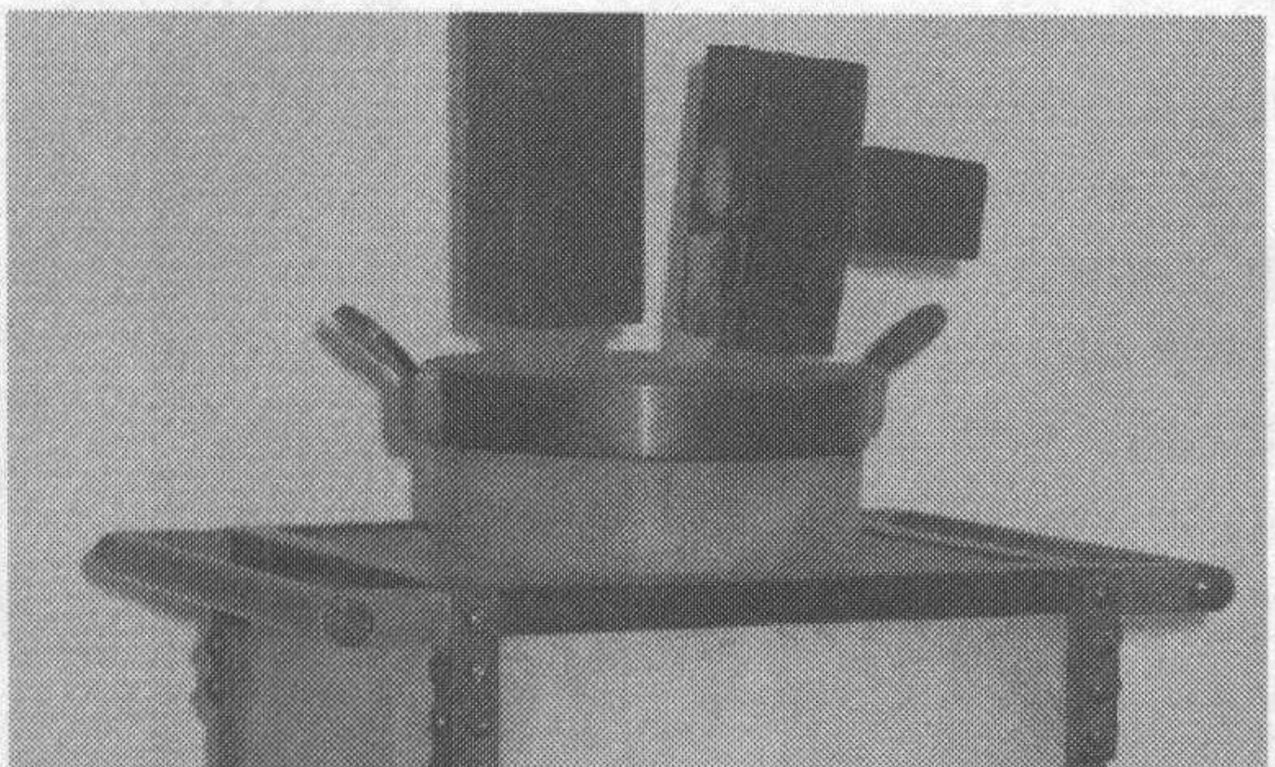


**Fig. 22** Electrolysis cell cut from a block of fluorite.
Document Henri Moissan Museum, Faculty of Pharmacy, University Paris V, Photo A. Tressaud.

returned to Saxony, where he was appointed doctor first in Joachimsthal[69] then in Chemnitz, where he ended his days in 1555. The location of the city on the eastern part of the Erzgebirge Mountains, one of richest mining centers of the time, allowed him to visit mines, deposits, and foundries as soon as he could escape his official duties. The discussions he had with experienced miners, particularly Lorenz Bermann or Wermann, provided the material for most of its future books. Besides *Bermannus sive de re metallica dialogus*, a treaty on the mining district,[70] successively appeared *De natura Fossilium*, always at J. Froben, an editor in Basel, *De natura eorum quae effluunt ex terra* and *De ortu and causis subterraneorum*, where he rightly attributed the origin of geological deposits by sedimentation of aqueous origin, and he described in detail the effects of erosion.[71] But the major work of Agricola, *De re metallica* (Fig. 23) was published after his death in 1556. He was the very first to account

GEORGII AGRICOLAE
DE RE METALLICA LIBRI XII. QVI-
bus Officia, Instrumenta, Machinæ, ac omnia denique ad Metalli-
cam spectantia, non modo luculentissimè describuntur, sed & per
effigies, suis locis insertas, adiunctis Latinis, Germanicisq; appel-
lationibus ita ob oculos ponuntur, ut clarius tradi non possint.
EIVSDEM
DE ANIMANTIBVS SVBTERRANEIS Liber, ab Autore re-
cognitus: cum Indicibus diuersis, quicquid in opere tractatum est,
pulchrè demonstrantibus.
BASILEAE M. D. LVI.
Cum Priuilegio Imperatoris in annos v.
& Galliarum Regis ad Sexennium.
LIVRE NEUF
A-B : Deux fourneaux C : Bassin supérieur D : Bassin inférieur
F : Les scories G : L'ouvrier prend de l'eau du baquet pour arroser les scories incandescentes
et les refroidir I : Racloir K : Minerai extrait
M : Perche

**Fig. 23** Portrait of Georgius Agricola.
Cover of the original Latin version of *De re metallica*, Basel 1530, with illustration of iron foundry operations using fluoride fluxes.

[69] Today Jáchymov in Czech Republic.

[70] Books of G. Agricola: "Bermannus, sive de re metallica dialogus" (1530); "From ortu and causis subterraneorum" (1546); "De natura effluent eorum quae ex terra" (1546); "From veteribus and novis metallis" (1546); "De natura Fossilium" (1546); "De re metallica" (1556).

[71] The fossils in question are minerals and what we call fossils today were regarded at the time as daring achievements of nature. Although the similarity between fossils and living organisms was widely observed, it was not until the early 18th century that it was recognized that these "stones" had been indeed living organisms. At Agricola's time, it was rather some of their medicinal properties, even magical, that were put forward, such as prescribing *lapis judaicus* powders (Echinoderms of Pentremites type) for stone disease, or fossil oysters to reduce lung inflammation.

for the use of fluorinated minerals as fluxes, such as fluorspar, and he even proposed to use the word "fluorine" ("fluores" in Latin). In his books, he related that miners of the Erzgebirge Mountains were aware that some stones could melt when heated, "Lapides qui facile igni liquescent," facilitating the extraction of metals by fusion of the ores (see "–'Stones that easily melt by heating' Lapides qui facile igni liquescunt"). Thanks to all these works, Agricola is recognized as the father of mineralogy. He found the best way to bring his work to posterity by structuring *De re metallica* into 12 books (or chapters), providing clear explanations of the various stages of techniques and processes, and asking an artist Basilius Wefring to illustrate the variety of situations in the most educational manner possible. We find in this book the foundation of natural science mostly based on experimentation that would be later called geology or earth science. He also added: "I have omitted all things that I had not seen by myself or read or heard from people of confidence." This view sometimes led him to question the classical authors like Aristotle and Pliny the Elder, whose statements were taken at that time as dogma. And if in his preface he quoted the ancient authors, it omitted some more recent scientists such as Avicenna (980–1037), Roger Bacon (1214–1294), Albertus Magnus (1193–1280), and even his contemporary and neighbor, Paracelsus (1493–1541). These omissions can be attributed to a certain distrust of the medieval alchemist tradition of Arab-Latin origin. Agricola's work, like that of Pliny to some extent, is marked by an obvious concern for writing down the memory of science and technology of the early 16th century, thanks to a comprehensive inventory of the human knowledge available on the subject in his time. This first scientific description of casting techniques initially written in Latin was quickly translated into many languages, including Chinese. His contemporaries, like Erasmus and Melanchthon, and later, Goethe, highlighted the decisive position he had held in the field of earth sciences. Closer to us, the first translation into English of *De re metallica* was proposed in the early 20th century by a mining engineer, the future US President Herbert C. Hoover, with the help of his wife, Lou Henri Hoover, a geologist and Latinist.[72] Herbert Hoover gave us this very wise definition of this great precursor: "He was the first to found any of the natural sciences upon research and observation, as opposed to previous fruitless speculation."

### "Stones that easily melt by heating" (Lapides qui facile igni liquescunt)

G. Agricola was the first to focus on the use of fluorinated minerals as fluxes, even creating the word "fluorine." In *De re metallica*, such a use is shortly reported; it is said that miners of Erzgzbirge Mountains name certain stones "fluores" (in Latin in the original text), that melt when heated ("Lapides qui facile igni liquescunt") facilitating the extraction of metals by fusion of the ores. These points were developed in many of his previous works, *Bermannus*, *Rerum Natura Metallicarum* and *De Fossilium Interpretation*. In *De Natura Fossilium*, he wrote: "Finally, there is now these stones I call, 'Stones that easily blend into the fire,' because thrown into a furnace, they start to melt…These are fluxes ('fluores sunt' in the original Latin text)."

In his first treatise on mining, *Bermannus*, *sive de Re Metallica* (dedicated to D. Erasmus in 1530), two scholars, Ancon and Naevius, are featured, in a method often used at the time,

[72] Detailed comments on *De Re Metallica* can be found in the first English translation of the Latin text of 1556 by H. C. Hoover and L. H. Hoover, The Mining Magazine, London (1912).

talking with Bermannus,[73] an engineer particularly skilled in mining. The conversation turns to the minerals found in the Erzgebirge Mountains. The way they describe the various types of stones shows the perfect knowledge of the works of ancient authors, especially Pliny's "Natural History." The appearance of these stones, the similarity with precious stones, and several other features perfectly coincide with the description of murrhine by Pliny. In addition, Agricola first released the melting properties of these rocks that had been known, apparently, for centuries in the development of glass, enamels, and other products. The description given by Bermannus perfectly matches that of fluorite crystals, but it is clear that in his day, it was not possible to differentiate between fluorinated minerals and those derived from quartz and silicates. Furthermore, fluorite deposits were mostly localized with oxides or sulfides. Nevertheless, it can be concluded that Agricola was the first to propose for these minerals the Latin word "fluores," borrowed from the German word "fluss," commonly used by the miners of that time, as shown in the dialog below between Bermannus and Naevius.

**Bermannus: A dialogue on mining**

NAEVIUS—What is this, Bermannus?

BERMANNUS—These are flows/fluxes ("fluorinated sunt" in the original Latin text). Let me take this word of another. Thus, our miners call it, in my opinion without impropriety. Because it looks like quite a molten and frozen material, just as ice, except that it has diverse and pleasant colors.

NAEV—These stones, Theophrastus says, the ἐχ συρροής, that is to say, formed by earthen runoff. These fluxes—I will use now such words—are red and appear identical in red raw silver, you have told us before.

BERM—At first glance, it is true, but it is not so, because fluxes are often quite translucent.

NAEV—These are carbuncles?

BERM—No, thereof in any case.

NAEV—How can we distinguish them?

BERM—First, because the colors do not shine in the eye as with carbuncles (any red gemstone, most often red garnets), although some parts are transparent. When they are opaque, they also differ in this respect. Finally, the fluxes of all types begin to flow as soon as they feel the heat,[74] while carbuncles do not liquefy.

NAEV—Your distinctions are clear.

BERM—You see here another type, a more diluted purple hue.

NAEV—This looks like the cheap amethyst so abundant in Bohemia.

BERM—This is certainly not dissimilar, so you can easily sell them—and they are sold—for precious stones for people who are not familiar with amethyst, if they are set in rings. But here's a third kind with a white shade.

NAEV—Looks like rock crystal.

BERM—A fourth species is yellowish, a fifth, ashy, and a sixth, almost black.

ANC—But what is the use of flux?

[73] A former companion of Agricola's studies in Italy, Jean Naevius was a doctor in Annaberg, then Joachimsthal; Nicolas Ancon, was also a physician, expert in Arabic medicine. Bermannus (from the German word "bermann," or miner), illustrates the advanced technology of the time and could have been Lorenz Bermann, master of mines, another friend of the author.

[74] Such observation has sometimes been confusing, resulting from relationships (promoted by Pliny the Elder) between heat and crystal colors. In the previous chapter, we explained that the ancients thought that minerals were created permanently, and the heat from the depths of Earth was required for the coloration of crystals. A *carbuncle* is any red gemstone, most often a red garnet.

BERM—It is customary to add them to the extraction of metals with fire. They make the melt much more fluid, indeed, and a stone taken from the "flint," as we have said, which is made not far from here in Breitenborn, near Schwarzenberg.[75] From these fluxes, further pigments for painters can also be drawn.

## 5 In search of the missing halogen, from the Renaissance to 1886

In the course of the 18th century, numerous observations showed that when an acid, for example, sulfuric acid, was added to a fluorspar sample and the mixture was gently heated, toxic fumes evolved, attacking glass containers. It is said that a Nuremberg glassmaker, Heinrich Schwanhard, had the idea in 1670 to use these properties for the production of glassware. Note that this technique is widely used to this day.

The first report written on this chemical reaction was published in 1725 by John George Weygand, relating to a recipe he inherited from Matthäus Pauli from Dresden, and the first scientific article on flußspat from Saxony was published in 1768 by Andreas Marggraf (1709–82).[76] In 1771, the Swedish chemist Carl Wilhelm Scheele (1742–86) began systematic work to discern the chemical nature of the crystals found in the fluorspar ores and their reaction mechanisms with acids. By adding sulfuric acid to fluorite crystals, he observed that the glass was also attacked by the formation of fumes. The dissolution of these fumes in water led to an acid solution that Scheele named "flußspatsäure," fluorspat acid, or fluoric acid. Added to carbonated water, a white precipitate ($CaF_2$) was isolated and dried with sulfuric acid.[77] So, C.W. Scheele was the first to identify the nature of fluorspar ore. Besides hydrofluoric acid, this scientist prepared and studied many other toxic gases such as $H_2S$, and HCN. Presumably, his untimely death was the result of a slow poisoning by these chemicals, because Scheele used to taste his preparations. We can note that this scientist, like all his contemporaries, thought that the acid was part of fluorspar ore. Even if the names proposed for this new acid (e.g., "acide fluorique" in France, "acido fluorico"in Italy) remind us today of the element fluorine, nothing was known at the time about the chemical nature of the constituents of the acid in question. Some critics even questioned Scheele on his results, suggesting that this acid was a derivative of the sulfuric acid used in the experiment. And even when Scheele showed long after his first experiments that the same results could be obtained by reaction of nitric or phosphoric acid on fluorspar, some others suggested that the resultant product was due to a modification of these acids.[78]

[75] In Saxony's Erzgebirge Mountains, south of Chemnitz and Zwickau.

[76] A. Margraff, Observation concerning outstanding volatilization of some of the stone species to which we give the names of Flosse, Flüsse, Flus-Spaht and also that of Hesperos, Memoirs Royal Academy of Sciences of Berlin, translated from German, Volume XXIV, 3–11, 1768.

[77] C. W. Scheele: Sämmtliche physische und chemische Werke. Nach dem Tode of Verfassers deutscher Sprache und in gesammelt herausgegeben Sigismund von Friedrich Hermbstädt, 2 Vols., Reprint of the edition of 1793, Niederwalluf, 1971, Vol. 2, pp. 3–31 (first published in 1771).

[78] B. Pelletier, Donadei L.: "Memoirs of lime phosphate", Ann. Chim. 7 (1790) 79.

The true nature of hydrofluoric acid began to emerge with the 19th century. When muriatic acid (HCl) was identified as a phase containing chlorine, a recently discovered element, it was recognized that oxygen (from the Greek, *ὀξύς* "generating acid") was not the essential component of acids, as was supposed before. By comparison, fluoric acid was thought to consist of hydrogen and another element with properties similar to those of chlorine. In 1809, when the discovery of sodium and potassium by the English chemist Humphrey Davy (1778–1829) was announced in France, André Marie Ampère (1775–1836) anticipated the existence of chlorine and fluorine as chemical elements, but did not publish his hypotheses. Struck by the analogies between muriatic acid (hydrochloric acid) and fluoric acid (hydrofluoric acid), he concluded that this was due to an element he first called oxyfluorique, and then fluorine, once he was convinced that hydrofluoric acid contained no oxygen. Among the letters he exchanged with Davy during the war raging between the two countries, on November 1, 1810, he even suggested the possibility of isolating the element fluorine by subjecting anhydrous hydrofluoric acid to electrolysis: "The question is whether electricity would decompose hydro-fluoric acid in its liquid form, when as much as possible water would have been removed, carrying hydrogen on one side and oxy-fluoric on the other side. The only drawback to fear is the combination of oxy-fluoric with the conducting piece. But, assuming that the oxy-fluoric was, as the oxy-muriatic, unable to combine with carbon, this latter element might be good enough conductor to be used successfully in such in experience."[79] In response in February 1811, Davy did not accept the existence of a single body proposed by Ampere, but considered it contained oxygen. "In the views that I have ventured to develop, neither oxygen, chlorine or fluorine are asserted to be elements." However, after 3 years of correspondence, Ampere left the fame to Davy as, in 1813, the latter announced the discovery of this new element.[80] An autobiographical note, however, established the priority of his discovery to Ampere, in fact well recognized by Davy: "During the period I was engaged in these investigations, I received two letters from M. Ampere of Paris, containing many ingenious and original arguments in favor of the analogy between the muriatic and fluoric compounds. M. Ampere communicated his views to me in the most liberal manner; they were formed in consequence of my ideas on chlorine and supported by reasonings drawn from the experiments of MM. Gay-Lussac and Thénard."

The quest for this new element occupied numerous researchers throughout the 19th century. A first step was the preparation of pure water-free hydrofluoric acid by Louis-Jacques Thénard (1777–1857) and Louis-Joseph Gay-Lussac (1778–1850). The product they produced spewed thick smoke into the air, rapidly dissolved glass, and caused very stubborn burns, a phenomenon that had been observed for a long time. Later, J.J. Berzelius (1779–1848) characterized ammonium fluoride.[81] During this period, several researchers paid a heavy price in search of fluorine.[82] G. and T. Knox suffered from severe fluorine intoxication, and the Belgian chemist P. Louyet died.[82] Around

[79] Correspondence of Grand Ampere, Gauthiers-Villars, Paris (1936) (containing the correspondence between the two scholars from 1810 to 1825).

[80] H. Davy, Philos. Trans. Royal Soc. London, **102** (1812) 352; ibid. **103** (1813) 263; ibid. **104** (1814) 62.

[81] Berzelius JJ., From the hydrofluoric acid, in Chemistry Treaty, Vol. 2, Brussels, 1833, p. 179.

[82] Rabuteau A. P. A., Toxicology Elements, Paris 1887; Roholm K, Fluorine Intoxication, Kopenhagen—London 1937.

1860, Jean Charles de Marignac (1817–94) synthesized and described in a surprisingly accurate manner the morphological characteristics of many crystals of anhydrous or hydrated salts such as fluorotitanates or fluorozirconate (see "J. C. de Marignac and the first synthetic fluoride crystals").[83] Henri Étienne Sainte-Claire Deville (1818–81) and Edmond Frémy (1814–94) also characterized many inorganic fluorides. In 1869, the great Russian chemist Dmitri I. Mendeleev (1834–1907) perfectly positioned this element in the periodic table that he had conceived.

A decisive step was taken when Frémy succeeded in preparing high-purity anhydrous hydrogen fluoride and $KHF_2$, also called Frémy's salt, "KFl·HFl" in the notation of that time.[84] G. Gore (1826–1904) determined its physical-chemical characteristics. It should be noted that in 1836 Frémy came close to the solution by electrolyzing salts based on molten calcium or potassium fluoride. Frémy has also long been credited with the paternity of this isolation because in 1856, he had already observed the evolution of a gas decomposing water with production of hydrofluoric acid: "It emerges from the neck of the platinum retort an odorous gas decomposing water to produce hydrogen fluoride, and which displaces the iodine content toward the halide: the gas seems to be fluorine."[85] However, at the temperature at which he operated, Frémy could not go further in the isolation of fluorine, and he never considered using $KHF_2$, presumably because of technological difficulties related to the high melting temperature of the compound, $T_m = 293°C$. So, in June 1886, Henri Moissan (1852–1907)[86] an alumnus of Frémy, finally succeeded in isolating fluorine, concluding this long chapter in the history of chemistry, as highlighted J. R. Partington (1886–1965), "The long isolation of fluorine was one of the master problems of inorganic chemistry."[87]

## Jean-Charles de Marignac and the first synthetic fluoride crystals

The singular character, outside of any school and away from scientific battles taking place in most European capitals, Jean-Charles de Marignac (1817–1894) taught all his life at the Academy of Geneva, later transformed to a university.[88] Marignac performed all his work alone without co-workers or assistants, mostly in the lab he had established in his personal home. Upon returning from his "post-doc" training in the Giessen laboratory of J. Liebig, Marignac

[83] A. D. Galissard de Marignac, Collected Works, Volumes I & II (1840–1887), Physics Society of Geneva, Masson, Paris (1890).

[84] JR Partington, The early history of hydrofluoric acid, Mem. Proc. Manchester Lit. Phil. Soc. **67** (1923) 73.

[85] Frémy E., Ann. Chim. Phys. **47** (1856) 5.

[86] Among the many publications of H. Moissan on fluorine and fluorine compounds, some may be mentioned: Recherches sur l'isolement du fluor, Annales Chim. Phys. 6ème série, t. XII (1887) 472. Nouvelles recherches sur le fluor, Annales Chim. Phys. 6ème série, t. XXIV (1891) 224. Fluorure double de chrome et potassium, Annales Chim. Phys. 7ème série, t. II (1894) 66. Le bifluorure de platine anhydre, C. R. Acad. Sci. **109** (1889) 807. Le Fluor et ses Composés, G. Steinhel Ed., Paris (1900) /Traité de Chimie Minérale, Masson Ed., Paris (5 volumes, 1904–1906).

[87] J. R. Partington, General and Inorganic Chemistry, MacMillan, London (1947).

[88] Information on the life and work of Marignac can be found in the "Book of the Centenary of the Ecole Polytechnique," Gauthier-Villars, Paris (1897), including a description of his scientific activities by E. Grimaux.

## 8.3 The story of Teflon and fluoropolymers

### 8.3.1 The discovery of Teflon

It was by accident that Teflon was discovered, but this discovery took place in a company that immediately understood the immense impact that this exceptional material could present. On April 6, 1938, Roy J. Plunkett (1911–94), a young chemist who was hired 2 years before by DuPont, assisted by Jack Rebok, failed to properly open a container in which a gas, tetrafluoroethylene (TFE: $C_2F_4$) was in contact with hydrochloric acid. When they finally had access to the inside, the researchers discovered a white powder, polyfluoroethylene [PTFE $(C_2F_4)_n$], better known today by its brand name Teflon (Fig. 36). R. Plunkett immediately understood the type of reaction that had just taken place, noting the same day in his notebook of experiences, "The white solid obtained was probably a product of polymerization."

### 8.3.2 Fluoropolymers: From military applications to hospital and kitchen uses

The exceptional properties of the product were quickly characterized: thermoplasticity, lubricating properties, high chemical inertness toward moisture, acids, bases, and various solvents; these led 1 year later to a patent on PTFE-based polymers. A major difficulty in synthesis, nevertheless, remained to be solved, because a spontaneous polymerization of

**Fig. 36** The discovery of Teflon by R.J. Plunkett (right) and his team (1938).

the monomer could lead to an explosion due to the high exothermicity of the reaction. DuPont chemists found a solution to the problem, but it was relatively expensive, and a potential market had to be clearly identified. WWII was ravaging the planet, and in the United States, a program called The Manhattan Project was launched in secret.

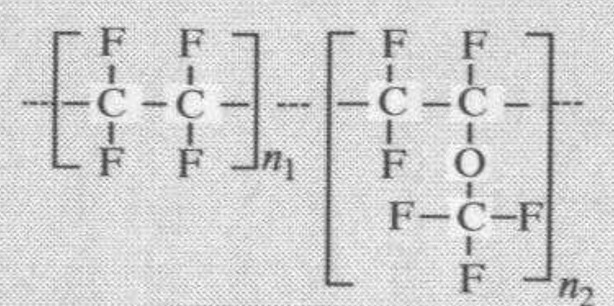
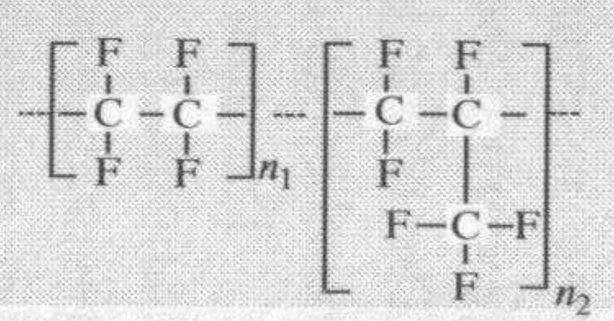
The project's final goal was to build an atomic bomb based on uranium isotope $^{235}U$, that is the only nucleide that could be rendered fissile with thermal neutrons. Among the different uranium compounds at highest oxidation state (VI+), the hexafluoride $UF_6$ can be obtained by burning tetrafluoride $UF_4$ in fluorine atmosphere gas ($F_2$) at high temperature. It is a solid at room temperature and sublimates at 56.5°C. An enrichment in $^{235}U$ could thus be possible via gaseous separation of the two fluorides $^{235}UF_6$ and $^{238}UF_6$. In such reactive conditions, the various parts of the equipment, valves, seals, etc., should be particularly inert. The DuPont Teflon corresponded exactly to these specifications. It thus became a highly secretive product, and renamed K-416. Teflon's entire production was reserved for various military projects and two-thirds of the Arlington production unit were allocated to the Manhattan project, the rest for other uses such as nose cone proximity bombs (thanks to its electrical insulating property and transparency to radar), fuel tank coatings (thanks to better resistance to low temperatures, etc.). It was only in 1944 that DuPont gave the name of Teflon to the PTFE product.

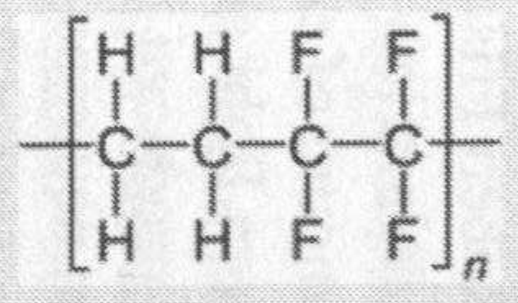
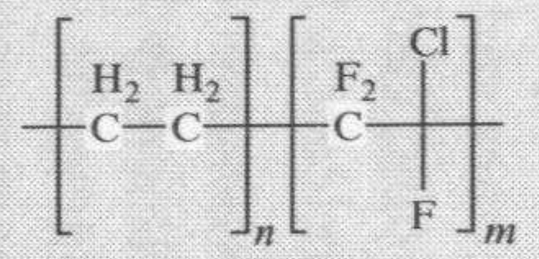
After the return of peace, the truly exceptional qualities of the material were quickly brought at the service of industry, medicine, and public well-being. Many new fluoropolymer families exhibiting specific features had appeared. As an example, the hydrophobic properties of fluoropolymers had given rise to new lines of clothing such as Gore-Tex-treated gear. The coating of extremely varied surfaces, fabrics, paper, leather, etc., by a film of these fluoropolymers rendered these materials hydrophobic (granting water impermeability) and/or oleophobic (spot-resistant). Many other applications are also concerned. Indeed, in the polymer chains, the substitution of fluorine for the hydrogen atoms improves many characteristics, increasing heat resistance and chemical resistance, delaying or inhibiting the spread of flame, lowering the critical surface tension, and increasing the fabric's insulating character. The effect is more marked as the degree of substitution of H by F is higher, and it reaches its maximum for polymers that contain only carbon and fluorine.

The main types of fluoropolymers are grouped in Table 5 with some of their applications. Their most outstanding properties, that is, high chemical resistance, excellent resistance in aggressive environments, lack of adherence, nonflammability, low dielectric constant, low temperature flexibility, high temperature stability, and low friction coefficient, make them unique materials for all branches of industry, such as chemicals, building, aeronautics, space, biotechnology, clothing, and medicine.[126] These exceptional properties explain why today, the range of fluoropolymers' uses is very wide in the aircraft and automobile industries, surface treatment of clothing, cardiovascular surgery, kitchen equipment, wire insulation for computer networks, and semiconductor manufacturing equipment (Fig. 37). In order to protect metal structures against atmospheric pollution, the treatment of the aluminum parts of the Louvre pyramid or the renovation of the Statue of Liberty in New York have used fluorinated polymers.

[126] Ameduri B., B. Boutevin, Well-Architectured Fluoropolymers, Elsevier, (2004); Ameduri B., Les (co) polymères fluorés,l'Actualité Chimique, N° **241**, 24–30 (2017).

**Table 5 Main types of fluoropolymers with applications**

| Fluoropolymer | Formula | Commercial brands | Major types of applications |
|---|---|---|---|
| PTFE—polytetrafluoroethylene | $[-CF_2-CF_2-]_n$ | Teflon, Fluon, Hostaflon, *Neoflon (ex-Kel-F)* | – Bearings, seals, high temperature electrical insulators, non-stick coatings and linings/coating cookware/sealing tape (renovation, Statue of Liberty)/solid lubricant/ deposits on razor blades/rainproof clothing, Gore Tex/ insulating fittings for electrical/high-voltage wiring/ computer mouse |
| PVF—polyvinyl fluoride | $[-CH_2-CHF-]_n$ | Tedlar | – Protecting films<br>– Gas tanks, solar panels, printed circuit |
| PVDF—polyvinylidene fluoride | $[-CH_2-CF_2-]_n$ | Kynar, Solef, *Hylar* | – Thermoplastic, highly resistant<br>– Piping, fittings and tanks, chemical industry/wire and piezoelectric elements insulation in electronics/ protection of metal parts in buildings (Louvre Pyramid)<br>– Biotechnology |
| PFA—perfluoroalkoxy |  | *Hyflon* | – Endurance to high bending/very good mechanical resistance to high temperatures<br>– Special tubings, moldings, coatings in chemical engineering equipment<br>– Transfer molding and extrusion |
| FEP—fluorinated ethylene propylene |  | Hostaflon | – Uses in extruded, molded, or injected forms |

| | | | |
|---|---|---|---|
| ETFE—tetrafluoroethylene and ethylene copolymer |  | *Tefzel, Fluon, Neoflon ETFE, Texlon* | – Use for very large surface panels: "Water Cube," Beijing, China, 2008 Olympics/20,000 $m^2$ window for "Tropical Islands" project, Brandenburg, Germany<br>– Protection of electrical equipment in extreme conditions/ resistance to high energy radiations<br>– Aerospace, nuclear energy |
| ECTFE—ethylene chlorotrifluoroethylene polymer |  | Halar | – Electronics and electrical chemical industries<br>– Cryogenic and aerospace applications |
| PCTFE—*polychlorotrifluoroethylene polymer* | $(-C\,F_2-CFCl-)_n$ | Voltalef | – Crystalline material (with crystalline levels ranging from 30% to 70%/high mechanical strength and low elongation. Cryogenics, polymer stable between −255°C and +150°C/extremely low permeability to gases<br>– Barrier material/electrical insulation in hostile climates: hot and humid climates, marine conditions |

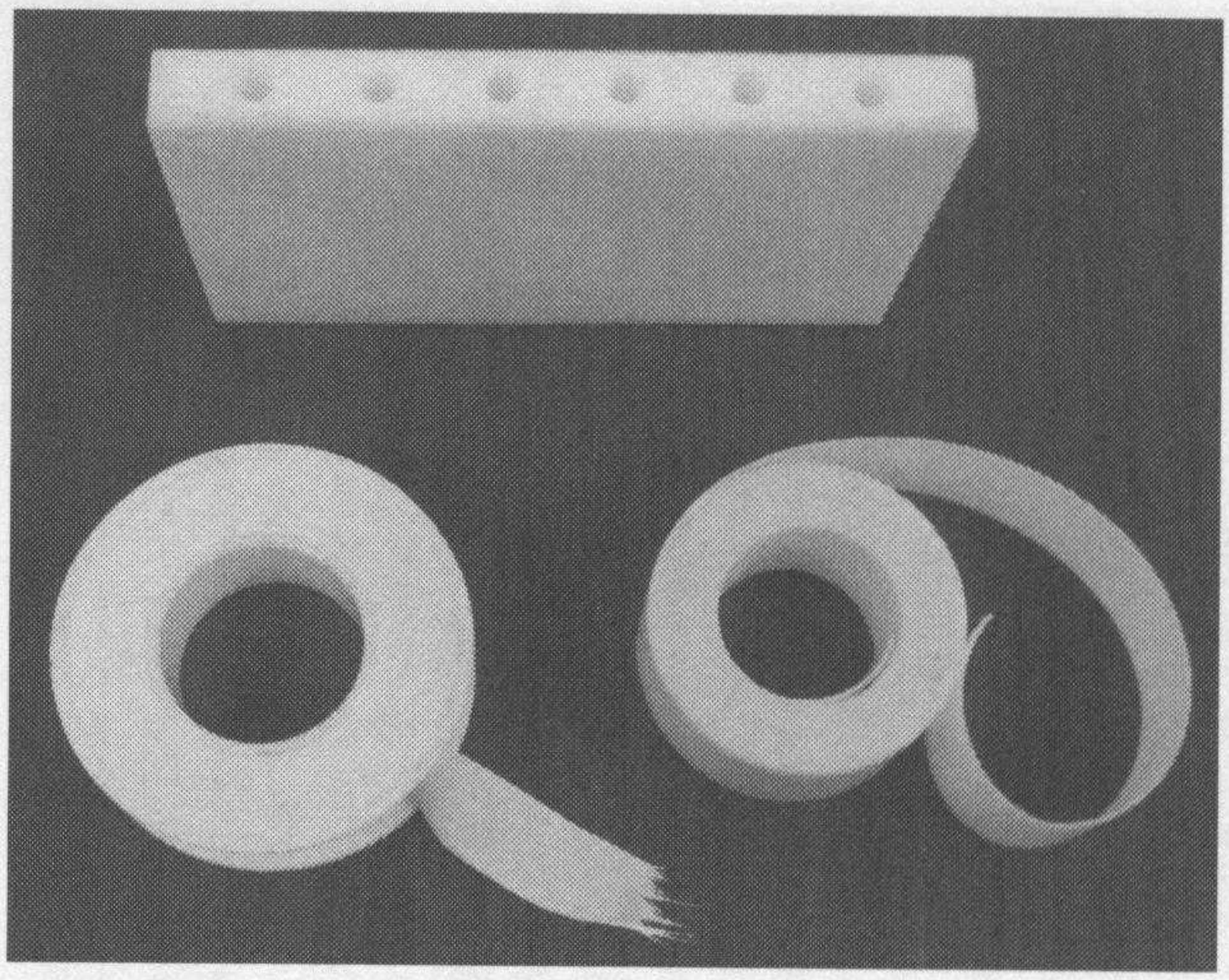


**Fig. 37** Various PTFE items.
Taken from https://hi.wikipedia.org/wiki/%E0%A4%9A%E0%A4%BF%E0%A4%A4%E0%A5%8D%E0%A4%B0:Teflon_items.jpg.

## 8.4 Fluorine, a decisive element in the nuclear cycle

### 8.4.1 The Manhattan project

During WWII, most discoveries involving fluorine and fluorine products had become top secret. So was Teflon, the Simons perfluorination electrochemical process which would be published in 1949, and of course, research on fluorine derivatives of uranium. The origin of the Manhattan Project back in 1939, when Niels Bohr came from Denmark to spend several months at Princeton University. With his American colleagues, Bohr discussed of the hypothesis of Lise Meitner and Otto Robert Frisch that the absorption of a neutron by a uranium nucleus would cause the separation of the latter into two approximately equal parts and would release a huge amount of energy, a phenomenon they called "nuclear fission." From discussions between Bohr and the Italian-born physicist Enrico Fermi, who studied ionizing radiation produced by the fragments of the U nucleus at Columbia University, came the idea that neutrons might be emitted during the process, leading to a nuclear-chain reaction. On August 2, 1939, Albert Einstein wrote a letter to President Roosevelt to sensitize him to the risks of Nazis developing this type of nuclear reaction in order to make destructive bombs. This correspondence prompted the president to set up a consultative committee for uranium, which, in 1942, yielded the Manhattan Project, led by R. Oppenheimer. This project was strengthened by the first nuclear reaction, self-sustaining chain conducted at the end of the year by the Fermi team at the University of Chicago. Independently, on May 1939, F. Joliot-Curie filed a patent for the use of nuclear energy to obtain explosive chain reactions.[127]

[127] F. Joliot Curie, H. Halban, L. Kowarski, Perfectionnement aux charges explosives, Invention Patent n° 971–324, Caisse Nationale de la Recherche Scientifique, Paris, May 4, 1939.

The realization of the atomic bomb required an enrichment of fissile $^{235}U$ isotope, the only U nucleide that could be rendered fissile with thermal neutrons. Natural uranium contains 99.28% $^{238}U$ isotope, with only about 0.71% $^{235}U$. With an enrichment of natural uranium into compositions containing between 3.5% and 4.5% $^{235}U$ could be obtained via gaseous separation of $^{235}UF_6$ and $^{238}UF_6$ uranium hexafluorides. Thus, a critical step was separating 235 and 238 isotopes. $UF_6$ can be obtained by burning tetrafluoride $UF_4$ in fluorine atmosphere gas ($F_2$) at high temperature. It sublimes above 56.5°C at atmospheric pressure. So, the diffusion of the gases through a porous material made it possible to differentiate the two types of $^{235}UF_6$ and $^{238}UF_6$ molecules of different sizes and masses. The lighter molecules diffused faster than the heavier, thus enriching the starting material to fissile isotope $^{235}UF_6$. The bomb ("Little Boy") dropped on Hiroshima August 6, 1945, was made of uranium 235. The uranium isotope separation can be achieved mainly by gaseous diffusion of uranium hexafluoride, but also via other techniques such as thermal diffusion and electromagnetic separation. The main work of separation took place in Oak Ridge. The uranium bomb was using a mechanism called a gun to obtain the critical mass of $^{235}UF_6$, that is, a mass of $^{235}U$ (the "bullet") was launched in a tube toward another $^{235}U$ mass, creating the mass critically needed for explosion.

## 8.4.2 Importance of fluoride materials in the nuclear cycle

Today, 60% of the world's production of $F_2$ is devoted to the production of $UF_6$ to fuel nuclear power plants. Therefore, elemental fluorine is part of what is commonly called the "nuclear fuel cycle," and thus constitutes an essential link for the preparation of electricity via power plants.

$$U_3O_8 \xrightarrow{HNO_3} UO_2(NO_3)_2 \xrightarrow{T^0} UO_3 \xrightarrow{H_2} UO_2 \xrightarrow{HF} UF_4 \xrightarrow{F_2} UF_6$$

$$UO_{2.0} \xrightarrow{+4HF,\,-2H_2O,\,400°C} UF_4 \xrightarrow{F_2,\,T>400°C} UF_6$$

For the manufacture of nuclear fuel, the fluorinated products occur at two levels: hydrogen fluoride, HF, transforms the ore concentrates into $UF_4$, and finally, it is an oxidation of $UF_4$ by fluorine gas which results in the production of uranium hexafluoride, $UF_6$, whereby the $^{235}UF_6$ enrichment can take place. In France, these processes are implemented by orano-AREVA, which ranks first in Europe and second in the world for the preparation of fluorine and number one in the world for the production of $UF_6$. Thus, thanks to its fleet of 58 nuclear reactors, France has achieved an energy independence rate close to 50%. The nuclear share of electricity generation is currently around 80%. The French nuclear fleet has 34 units of 900 MW, 20 units of 1300 MW, and 4 units of MW 1450; the last unit was commissioned in 1999 to Civaux.[128] Fig. 38 shows the place of fluorine at different steps of the nuclear fuel cycle:

[128] H. Groult, F. Lantelme, D. Devilliers, C. Belhomme B. Morel, F., JP Nicolas, J.P. Caire, Fluoride, Elec trochemical synthesis of fluorine from 1886 to 2006: fluorine, a key-element for nuclear energy, Special issue devoted to Fluor and Fluorinated Materials, Actualité Chimique 144–147, (2006), pp. 40–46.

# The uranium cycle in the nuclear industry

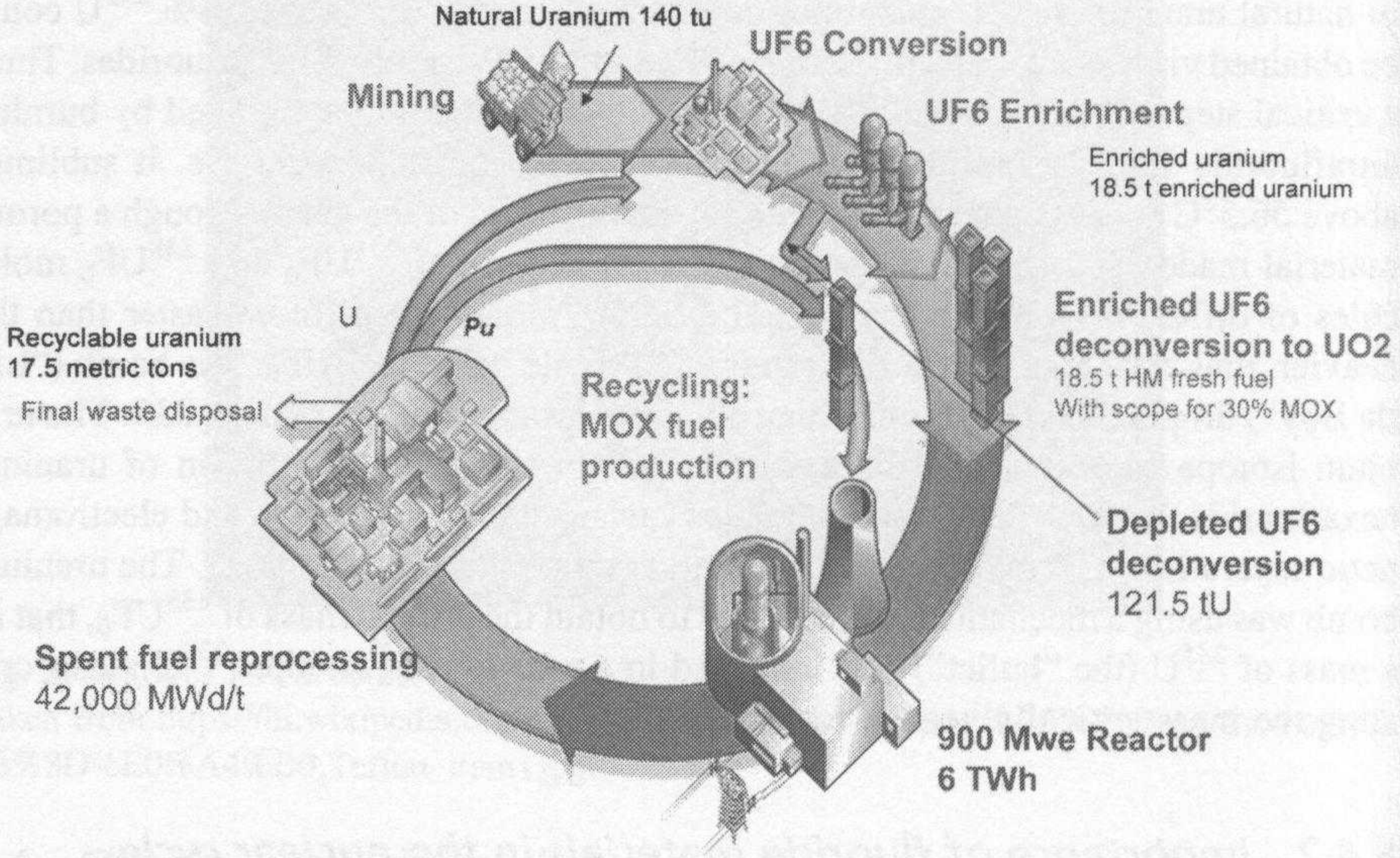



**Fig. 38** Contribution of fluorine and fluoride components in the nuclear cycle [*credit orano-AREVA*].

conversion to $UF_6$ and enrichment, enriched $UF_6$ converted into $UO_2$, and depleted $UF_6$ deconversion. It should be pointed out that civilian nuclear programs—although sometimes criticized—allow us today to limit the depletion of fossil energy resources.

A think tank was initiated several years ago to propose new types of nuclear reactors: the Generation IV nuclear reactors. A "Generation IV International Forum" (GIF) was initiated in 2000.[129] It is an international collective representing governments of 14 countries where nuclear energy is significant now and also seen as vital for the future. Most countries are committed to joint development of the next generation of nuclear technology.[130] The motivations for the project include goals such as improved safety, sustainability, efficiency, and cost.

Among the various types of Generation IV nuclear reactors, are thermal reactors, very-high-temperature reactors (VHTR), molten-salt reactors (MSR), supercritical-water-cooled reactors (SCWR), gas-cooled fast reactors (GFR), sodium-cooled fast reactors (SFR), and lead-cooled fast reactors (LFR).

[129] Locatelli, Giorgio; Mancini, Mauro; Todeschini, Nicola (2013-10-01). "Generation IV nuclear reactors: Current status and future prospects". Energy Policy 61: 1503–1520. "GIF Portal—Home—Public." www.gen-4.org.

[130] The original members of GIF were Argentina, Brazil, Canada, France, Japan, South Korea, South Africa, the UK, and the USA. The agreement was subsequently signed by Switzerland, Euratom, China, Russia, and Australia.

In molten salt reactors, the nuclear fuel may be solid or dissolved in the coolant. The thorium molten salt reactor used mixtures of LiF-$BeF_2$-$ThF_4$-$UF_4$ as fuel. The initial composition was very low in U, with a composition of 77.5% LiF, $ThF_4$ 18.7%, and 3.8% $UF_4$. One of its advantages was that a mixture of uranium-238 was implemented in order to make sure that recovered uranium would not be weapons grade. The most well-known molten salt breeder reactor was built at the Oak Ridge National Laboratory and used LiF-$BeF_2$-$ThF_4$-$UF_4$ (72-16-12-0.4 (%)) mixtures as fuel. It was moderated by graphite with a 4-year replacement schedule. The secondary coolant was NaF-$NaBF_4$. Its peak operating temperature was around 705°C.[131] Despite its success, the MSR program closed down in the early 1970s in favor of the liquid metal fast-breeder reactor (LMFBR), after which, research stagnated in the US. Regular GIF reports are available, including the 2016 report.[132] On January 2016, the US Energy Department announced new investments in advanced nuclear power reactors.[133]

[131] Energy From Thorium's Document Repository: The Use of Thorium in Nuclear Power Reactors. WASH 1097, ORNL.gov (http://www.energyfromthorium.com/pdf/ http://moltensalt.org/references/static/downloads/pdf/WASH-1097.pdf.

[132] H. Boussier, S. Delpech, V. Ghetta et al.: The Molten Salt Reactor (MSR) in Generation IV: Overview and Perspectives, GIF Symposium Proceedings, 2012 Annual Report, NEA No. 7141, pp. 95 [3]. GIF Portal—Annual Reports https://www.gen-4.org/gif/jcms/c_92757/gif-annual-report-2016.

[133] US Department of Energy. Retrieved January 16, 2016. https://www.energy.gov/articles/energy-department-announces-new-investments-advanced-nuclear-power-reactors-help-meet.

# Acknowledgments

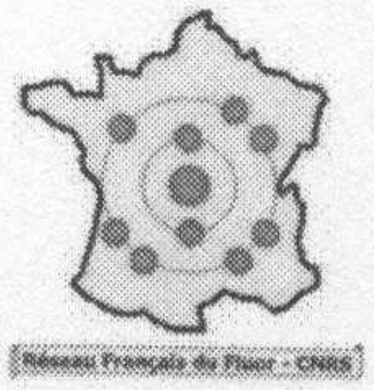
These years spent tracking down new fluorinated materials could not have been possible without two great scientists, Paul Hagenmuller (1921–2017), one of the initiator of solid-state chemistry in France and worldwide, who welcomed me in his group in Bordeaux, one day of September 1964, and Neil Bartlett (1932–2008), discoverer of noble gas compounds, in whose laboratory I spent my postdoctoral time at U. C. Berkeley and who remained my mentor until his early disappearance.

I am indebted to CNRS for allowing me to realize my passion for research since 1966, and more recently to the National Program: "*French Fluorine Network*", to have made me aware of new scientific horizons.

Many thanks to all my colleagues of ICMCB-CNRS, from the oldest times: R. de Pape, J. Portier, J. Grannec, L. Lozano, L. Fournès, J. Darriet, J.P. Chaminade, J. Claverie, J. Etourneau, J.M. Dance (†), to more recent ones: A. Demourgues, M. Gaudon, B. Chevalier, E. Durand, who shared my joys of discovery, to all my post-docs and students who have helped to keep intact my energy and my scientific curiosity.

Also to all my French and foreign colleagues who, through constant and fruitful exchanges, opened me to new perspectives by abolishing borders, in particular H. Groult (Paris), but also D. Babel (Marburg), K. Christe (Los Angeles), L.P. Demyanova (St Petersburg), J. B. Goodenough (Austin), M. Feist (Berlin), I.N. Flerov (Krasnoyarsk), R. Hagiwara (Kyoto), E. Kemnitz (Berlin), A. Kharitonov (†) (Moscow), M. Leblanc (Le Mans), D. Lutar (†) (Ljubljana), D. Meshri (Catoosa), V.N. Mitkin (Novosibirsk), T. Nakajima (Toyota), P. Nuñez (La Laguna), H. Roesky (Göttingen), G. Schrobilgen (Hamilton), H. Touhara (Ueda), N. Watanabe (†) (Kyoto), J. Winfield (Glasgow), B. Žemva (Ljubljana).

So many thanks to my wife Viviane, to Laurent and Mathieu, and all my family who have often had to suffer from my passion for research. And finally to everyone who has made my life more enjoyable.



# Fluorine

## A Paradoxical Element

### Progress in Fluorine Science Series

dited by Alain Tressaud

*n overview of fluorine and fluorinated products from discovery of the element, major milestones in chemistry nd applications, environmental and health impacts, and future potential for fluorine science*

Describes background and contextual information regarding the history, development of understanding and applications of this important element

Explores the impacts of fluorine, both positive and negative, in the environment and in biological systems

Includes applied, real-world information from agencies such as the Centre National de la Recherche Scientifique (CNRS), National Aeronautics and Space Administration (NASA), HWS and Department of Health (DOH), World Health Organization (WHO), Intergovernmental Panel on Climate Change (IPCC), U.S Geological Survey (USGS), and the United Nations Framework Convention on Climate Change (UNFCCC)

*luorine: A Paradoxical Element* deals with the complex links between fluorine, humanity, and the environment his unique resource is divided into three main sections which explore the history of the element fluorine nd stages of the development of fluorinated products; awareness of the importance of this element in our nvironment (both in the atmosphere and lithosphere) and the issues surrounding it; and finally, recent pplications of fluoride products in medicine, pharmacology, and in our daily lives.

ngaging the reader with interesting figures and accessible language, *Fluorine: A Paradoxical Element* serves as valuable reference for chemists and related scientists working in materials, photonics, medicine, pharmacy, iotechnologies, toxicology, and environmental science. Written by a leading expert in the field, Professor Alain Tressaud, this book is the latest volume in the Progress in Fluorine Science series, which includes the work of highly-respected volume editors and contributors from both academia and industry, bringing valuable nd varied content to this active field.

**Alain Tressaud** is the Emeritus Research Director at ICMCB-CNRS, Bordeaux University. He is president of he European Academy of Science in Brussels and member of several European academies. He founded and chaired the French Network on Fluorine Chemistry, sponsored by CNRS, until 2008. He has received several awards, including the CEA Award of French Academy of Sciences (2008), the Fluorine Award of the American Chemical Society (2011), and the International Henri Moissan Prize (2012). His scientific interest covers various fields, including synthesis, physical chemical characterizations, applications in fluorine chemistry, solid state chemistry, and materials sciences. His work also deals with surface modification of materials and intercalation chemistry. Professor Tressaud's scientific production includes more than 360 papers in international journals, 20 book chapter contributions, and 12 internationalized patents. He has also edited several books in his role as editor-in-chief of the series *Advances in Fluorine Science* (2006) and *Progress in Fluorine Science* (2016) with Elsevier.

ELSEVIER

elsevier.com/books-and-journals

ISBN 978-0-12-812990-6